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III. ON THE SO CALLED DIOXYMALEIC ACID.

By W. S. Hendrixson.

Presented May 28, 1889.

Several years ago Bourgoin[*] announced the discovery of two new acids which he had obtained by replacing the bromine of brommaleic and dibrommaleic acid by hydroxyl, and which he therefore called oxymaleic and dioxymaleic acid. Although the experimental evidence as to the existence of these acids was very slight, and their assumed structure wholly anomalous, they soon found place in many text-books.

In 1886, at the suggestion of Fittig, the work of Bourgoin upon oxymaleic acid was repeated by Scherks,[†] who found that his statements were without foundation, and that brommaleic acid in aqueous solution was not in the least attacked by argentic oxide, even at 100°. Scherks further concluded that Bourgoin's statements concerning his dioxymaleic acid must also be incorrect, because the dibrommaleic acid which he used he claimed to have made from his tribromsuccinic acid, an acid which could not be formed under the given conditions, as shown by Fittig and Petri,[‡] or if formed would at once be decomposed into dibromacrylic acid and carbonic dioxide. This conclusion of Scherks seems hardly justified by Bourgoin's statements. The dibrommaleic acid which he used undoubtedly was made by the action of aqueous bromine upon succinic acid, and, while his material may have been far from pure, the question of its identity is in no way affected by his erroneous assumption that it had been formed by the decomposition of tribromsuccinic acid. In any case the subject seemed to demand a more careful investigation. At the suggestion of Prof. H. B. Hill, I have, therefore, repeated Bourgoin's work upon dioxymaleic acid, and find that decomposition is in this case readily effected, but that the product formed is not dioxymaleic acid.

The dibrommaleic acid needed for this investigation was made by the oxidation of mucobromic acid with cold fuming nitric acid, a method which had already been found in this laboratory to be much more advantageous than the methods previously described. Mucobromic acid was dissolved in cold fuming nitric acid, and the nearly saturated solution allowed to stand for several days at ordinary temperatures. When the mixture had completely solidified, the nitric acid was expelled by gentle heat, and the dry residue distilled from a small retort. In order to obtain a perfectly pure product, the distillate was dissolved in water, neutralized with baric carbonate, and the baric dibrommaleate precipitated by the addition of alcohol. The barium salt was then converted into the sodium salt, and from this the silver salt was made by precipitation with argentic nitrate.

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[*] Bull. de la Soc. Chim., xix. 482; xxii. 443.

[†] Ann. d. Chem. u. Pharm., ccvii. 223.

[‡] Ibid., cxcv. 70.

According to Bourgoin, dioxymaleic acid is formed by heating argentic dibrommaleate with water to 150°. On opening the tubes after heating for five hours he found that carbonic dioxide escaped, that argentic bromide had been formed, and that the liquid in the tubes was distinctly acid. On the addition of argentic nitrate to this acid solution carefully neutralized with ammonic hydrate he obtained a white insoluble silver salt, which gave on ignition a residue closely agreeing with the weight of metallic silver required by the formula $Ag_2C_4H_2O_6$. He found the acid to be a white crystalline solid, which was readily soluble in water and alcohol, and barely soluble in ether. With the alkalies and alkaline earths it formed readily soluble salts, and showed itself to be non-saturated in that it was capable of fixing hydrogen and bromine. Bourgoin gives, however, no analytical results whatsoever except the one already mentioned.

On following closely the directions of Bourgoin, I found that the argentic dibrommaleate had been almost completely decomposed, and that at least 95 per cent of the theoretical amount of argentic bromide had been formed. The liquid in the tubes was strongly acid, but the carbonic dioxide which escaped was by no means insignificant in quantity. Although the aqueous solution gave a crystalline precipitate with argentic nitrate after careful neutralization with ammonic hydrate, it was thought advisable to distil the liquid with steam before preparing salts for analysis, since it was found that the acid volatilized readily under these conditions. The acid distillate was neutralized with calcic carbonate, the silver salt precipitated by the addition of argentic nitrate to the concentrated solution, and recrystallized from hot water. The silver salt thus obtained closely resembled argentic acetate, and its identity was established by analysis.

I. 0.4677 grm. of the air-dried salt gave 0.5249 grm. AgBr.

II. 0.2263 grm. of the air-dried salt gave 0.1465 grm. Ag.

III. 0.2056 grm. of the salt dried over sulphuric acid gave 0.1082 grm. CO_2, 0.0330 grm. H_2O, and 0.1327 grm. Ag.

	Calculated for $AgC_2H_3O_2$.	Found.		
		I.	II.	III.
Ag	64.67	64.46	64.73	64.54
C	14.37			14.35
H	1.80			1.78

The barium salt was also made by neutralizing the acid distillate with baric carbonate. The salt obtained on evaporation was either recrystallized from water, or precipitated from a concentrated aqueous solution by alcohol. I failed to find any definite statements as to the composition of the salt thus precipitated by alcohol, but experiments of my own showed that it contained one molecule of water like the salt crystallized from water.

I. 1.1456 grm. of the air-dried salt lost at 150° 0.0780 grm. H_2O.
II. 0.9187 grm. of the air-dried salt lost at 125° 0.0609 grm. H_2O.
III. 0.4561 grm. of the air-dried salt gave 0.3899 grm. $BaSO_4$.
IV. 0.6868 grm. of the air-dried salt gave 0.5841 grm. $BaSO_4$.

	Calculated for $Ba(C_2H_3O_2)_2 . H_2O$.	Found.			
		I.	II.	III.	IV.
H_2O	6.59	6.80	6.62		
Ba	50.18			50.25	50.02

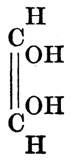
0.8554 grm. of the salt dried at 125° gave 0.7811 grm. $BaSO_4$.

	Calculated for $Ba(C_2H_3O_2)_2$.	Found.
Ba	53.73	53.69

It thus appears that acetic acid is formed in the decomposition of argentic dibrommaleate by water at 150° and the reaction may be expressed by the equation:

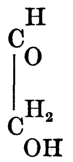
$$Ag_2C_4Br_2O_4 + 2\ H_2O = 2\ AgBr + CO_2 + C_2H_4O_2.$$

The weight of baric acetate which was obtained from the distilled liquid amounted to about 60 per cent of the theoretical yield required by this equation, while 85 per cent of the theoretical amount of free acid, calculated as acetic acid, was found by direct titration of the contents of the tubes. The higher result in the latter case may in part have been due to incomplete expulsion of the carbonic dioxide, but the most careful search failed to show that any well defined organic acid except acetic acid had been formed in the reaction. Dibrommaleic acid therefore yields, under the conditions prescribed by Bourgoin for its conversion into dioxymaleic acid, carbonic dioxide and acetic acid. The facts observed give no certain information as to the mechanism of the reaction. If it is assumed that the body



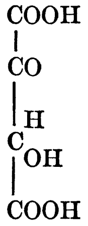
$$HC(OH)=C(OH)H$$

is first formed, it would pass at once into the aldehyde alcohol



$$HC(O)-CH_2OH$$

from which acetic acid would then be formed, precisely in the same way that tartronic acid is formed from dibrompyruric acid,* or from dioxytartaric acid.† It is more probable, however, that the ketone acid



$$COOH-CO-CH(OH)-COOH$$

is the first product, and that this passes into acetic acid in a similar way through the loss of carbonic dioxide.

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* Grimaux, Bull. de la Soc. Chim., xxvii. 440.

† Kékulè, Ann. Chem. u. Pharm., ccxxi. 230.